Positron-Molecule Bound States and Positive Ion Production

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ABSTRACT

We have studied the interaction of low-energy positrons with large molecules such as alkanes $(C_n H_{2n+2})$.[1] These data provide evidence for the existence of long-lived resonances and bound states of positrons with neutral molecules. The formation process and the nature of these resonances are discussed. We have observed the positive ions produced when a positron annihilates with an electron in one of these resonances,[2] and this positive-ion formation process is discussed. This paper is a review of the current state of our understanding of these positron-molecule resonances and the resulting positive ion formation.[3] We also discuss a number of outstanding issues in this area.

INTRODUCTION

We have conducted experiments to accumulate and store large numbers of positrons in an electrostatic trap.[4] This has allowed us to study, in a sensitive way, the low-energy inelastic processes occurring between positrons and neutral atoms and molecules. In the course of these experiments, we have found that the addition of large organic molecules to the trap increases the annihilation rate of the positrons to the extent that this annihilation process cannot be explained by direct collision phenomena alone. From a systematic study of the interaction of positrons with alkane molecules as a function of molecular size, we have demonstrated the existence of long-lived resonances and bound states of the

positrons and these neutral molecules. A model of the formation of these resonances is discussed. Annihilation rate data are presented for a variety of chemical species in order to test various aspects of the model. At present, there are discrepancies between the model and the experiments, and we do not have a complete picture of the bound-state formation process. One consequence of the bound states is that they naturally provide an efficient mechanism for the production of positive ions when the positrons annihilate with an electron on the molecule. We have directly observed the ions produced in this manner, and we discuss this phenomenon.[2]

THE POSITRON TRAP[4]

The experimental arrangement is shown schematically in Fig. 1. Positrons from a ^{22}Na radioactive source are moderated to 2 eV by a single-crystal, tungsten, transmission moderator. They are incident from the right onto the configuration of potentials and neutral-gas pressure shown. The background gas used to trap the positrons is molecular nitrogen. The gas pressure is adjusted so that, in one transit through the trap, the positrons make inelastic, electronic-excitation or ionizing collisions with the N_2 and are trapped in regions I, II, and III. The potentials are adjusted so that subsequent vibrational excitation of the N_2 traps the positrons, first in regions II and III in about 1 ms (transition B in Fig. 1), and then in region III in less than 0.1 s (transition B'). The N_2 pressure in region III (the confinement volume) is typically 1-5 x
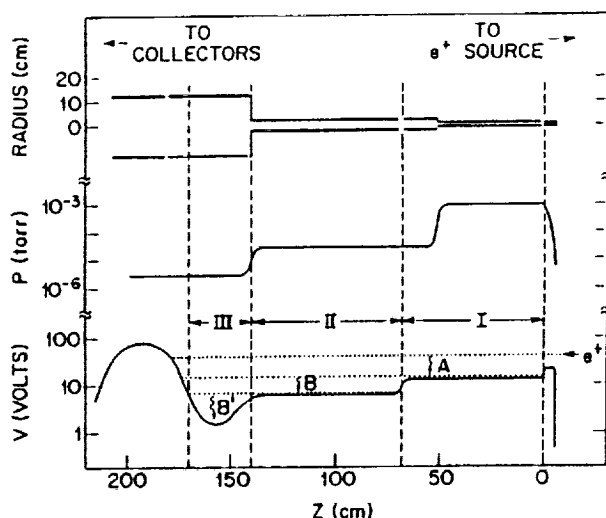
FIG. 1. A schematic diagram of the three-stage positron trap, including the electrode structure, nitrogen gas pressure, and the electrostatic potential profile. There is an axial magnetic field in the Z direction. The positrons lose energy by electronic excitation and/or ionization of the N_2 (labeled A) or by vibrational excitation of the N_2 (B and B').

10^{-6} Torr, and the base pressure of the vacuum system is less than 3×10^{-8} Torr. The magnetic field in region III is in the range from 250 to 800 G. For the work presented here, the total number of trapped positrons is always less than 1×10^4.

After variable fill and storage times, the contents of the trap are dumped onto an arrangement of annular collectors located at $Z = 265$ cm in Fig. 1, and the resulting 511-keV γ-ray annihilation radiation is monitored with a NaI detector and pulse-counting electronics. By suitable biasing of the collector plates, either the total number of positrons in the trap or the radial distribution of the positrons can be measured. We have also studied the confinement of electrons in the same geometry.

We have measured the time dependence of the cooling of the positrons in the trap. When the potential difference between regions II and III is set at 8.3V, the characteristic time that the positrons remain in regions II plus III, before being trapped in region III, is 20 ms. The

positrons entering region III are found to cool to energies ~1eV in less than 0.1 s. It is likely that, in this range of energies, the positrons cool via vibrational excitation of N_2. The subsequent cooling of the positron gas occurs at a slower rate, and it is either due to rotational excitation of N_2 molecules or to elastic scattering with N_2. The temperature of the positron gas in this range of energies is measured by a "magnetic beach" energy analyzer.[5] This technique involves measuring the number of positrons reaching the collector as a function of a retarding potential with and without an increased magnetic field between region III and the collector. This added magnetic field acts as a magnetic mirror to reflect positrons with energies, $\langle E_\perp \rangle$, perpendicular to the field. The shift in the retarding potential curves is a measure of $<E_\perp>$. Since the positrons make frequent collisions with N_2 molecules, they are expected to have an isotropic velocity distribution in region III. Thus, we can infer the average energy $<E> \equiv (3/2) <E_\perp>$.

Shown in Fig. 2 are data for $\langle E \rangle$ as a function of storage time for short filling times (~50-100 ms), at a magnetic field B_0 of 430 G. The N_2 gas pressure for this data was 1.5×10^{-6} torr. For these data, the corresponding positron confinement time in the trap was greater than 20 sec. The characteristic time for cooling in the range of energies shown in Fig. 4 is 0.6 s. The data are plotted by subtracting the kinetic energy of 0.038 eV expected for positrons at room temperature. The fact that the data can be fitted by a single straight line confirms that the positrons are cooling to room temperature. The observed cooling rate is found to be proportional to the N_2 pressure.

In order to study the ions formed in the trap, a two-stage channel plate, electron multiplier was placed 100 cm away from the center of region III (i.e., at $Z = 260$ cm in Fig. 1), and the electrodes surrounding region III were biased at +5 V to accelerate the ions toward the channel plate. After suitable fill and storage times, the potential barrier located near 195 cm in Fig. 1 is lowered, and the contents of the trap are dumped onto the channel plate. The channel plate is biased at -2400 V, providing near-unity detection efficiency for ions with masses in the range studied (i.e., 10-150 amu). When this ion signal is measured as a function of time delay after the trap is dumped, we have a simple, time-of-flight mass spectrometer.
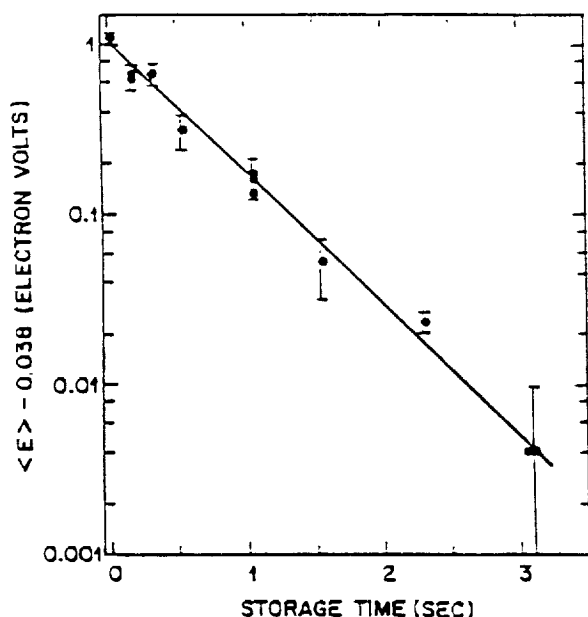
$C \cdot 4$

FIG. 2. The total, average energy of the positrons $\langle E \rangle$ minus their energy at room temperature as a function of storage time. The straight line corresponds to a characteristic cooling time of 0.6 s. The positrons cool to nearly room temperature n about 3 s.

POSITRON ANNIHILATION IN THE PRESENCE OF LARGE MOLECULES[1]

When no special precautions were taken in the treatment of the vacuum chamber, the characteristic confinement time, τ, of positrons stored in the trap was found to be of the order of 1 s, as compared to confinement times of 100 s for electrons, even when the total number of stored electrons was of the order of 1×10^9, where space-charge effects tend to enhance the radial diffusion. It was the surprisingly short positron confinement time which led to the discovery of the positron-molecule resonances described here. Measurement of the radial distribution of the positrons indicates that, under

these circumstances, they do not diffuse appreciably on time scales of the order of 1 s but are confined in the central region of the trap. Thus, we concluded that they annihilate before diffusing to the walls. The positron confinement time, τ, is *insensitive* to the N_2 gas pressure, so that the annihilation does not appear to involve the N_2. The key observation was that the positron confinement is extremely sensitive to the history of the vacuum chamber. For example, mild heating of the chamber wall decreases τ, while the introduction of a liquid-nitrogen-cooled surface near region III increases τ from 1 to 150 s. This led us to the conclusion that impurity molecules in the vacuum system were involved.

Previous studies indicate that positron annihilation is well understood for a number of gases, including nitrogen and hydrogen, but is not understood in other gases such as methyl chloride and butane.[6] We therefore introduced specific impurities into the vacuum system to investigate this effect. We found that water molecules had no effect on τ, but that τ was, for example, extremely sensitive to the oil from our pumps, to the extent that 1×10^{-9} Torr of oil could explain the observed containment time.

We chose to study this effect systematically with linear, hydrocarbon molecules (alkanes) of the form $C_n H_{2n+2}$, for several values of n ranging from 4 to 16. Shown in Fig. 3 are data for the positron confinement as a function of time when small amounts of butane ($C_4 H_{10}$) and heptane ($C_7 H_{16}$) are introduced into the vacuum chamber.[7] The number of trapped positrons, $N(t)$, as a function of the storage time, t, can be described by a simple exponential, $N(t) = N(0) \exp(-t/\tau)$, with τ a strong function of the pressure of the alkane species added. As shown in Fig. 3, heptane has a much greater effect on τ, per molecule added, than does butane. Similar results were obtained for all of the alkane molecules studied -- the larger the molecule, the shorter the observed annihilation time per unit pressure of the added alkane species.

In order to analyze the data quantitatively, we assume that the increase in the annihilation rate is proportional to the increase in pressure, ΔP, of the added gas species. Thus,

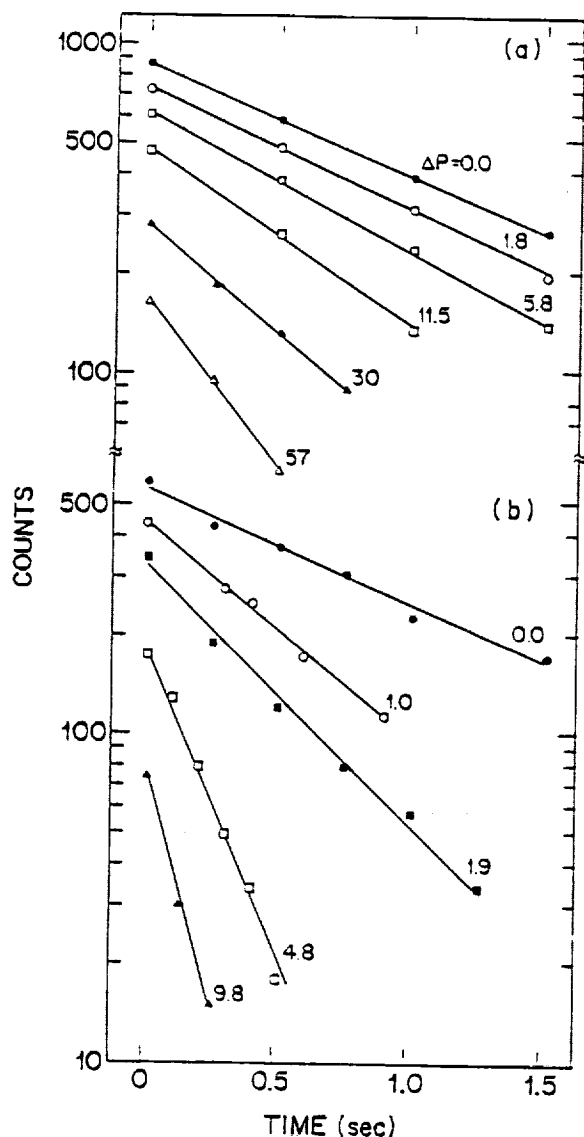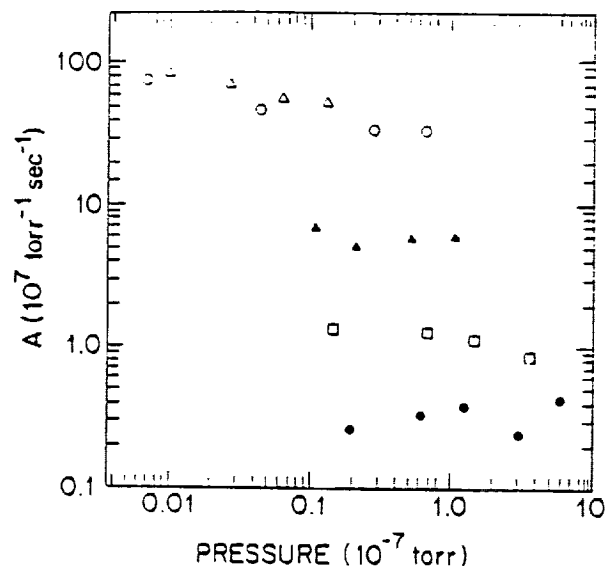$$\tau^{-1} = \tau_0^{-1} + A \, \Delta P, \qquad (1)$$

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FIG. 4. The annihilation rate per unit pressure, A, of the positrons as a function of the added pressure of alkane molecules: filled circles, butane (C_4H_{10}); open squares, pentane (C_5H_{12}); filled triangles, heptane (C_7H_{16}); open circles, dodecane $(C_{12}H_{26})$; and open triangles, hexadecane $(C_{16}H_{34})$.

FIG. 3. Positron confinement as a function of storage time when (a) butane (C_4H_{10}), and (b) heptane (C_7H_{16}), are introduced into the containment volume (region III) in the presence of 4.4×10^{-6} Torr of N_2 gas. The pressure, ΔP, of the added alkanes is in units of 1×10^{-8} Torr.

where τ_0 is the lifetime of the trapped positrons with no alkanes added, and A is a constant. Shown in Fig. 4 are data for several of the alkane molecules. In each case, A is approximately independent of gas pressure, as assumed. The most striking feature of the data is the large increase in A when the size of the alkane molecule is increased.

The annihilation rate, Γ, of positrons in collision with atoms or molecules is historically written in terms of the Dirac annihilation rate for positrons in a free-electron gas;[6] $\Gamma = Z_{eff}\rho\pi c r_0^2$, where c is the speed of light, r_0 is the classical radius of the electron, ρ is the number density of the gas, and Z_{eff}, which is the effective number of electrons per molecule, takes into account details of the electronic structure. In Fig. 5, we use our measured data for A to infer Z_{eff}/Z as a function of the number of electrons, Z, in the alkane molecule. The data indicate that Z_{eff} for dodecane and hexadecane is approximately 2×10^6. Also shown in Fig. 4 are data for Z_{eff} for the smaller alkane molecules measured in dense gases.[6]

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Figure 5 shows an increase in the annihilation rate of over three orders of magnitude when the size of the molecule is increased, and it also shows that this effect is not due simply to an increase in the number of electrons.

This large enhancement in the annihilation rate is not likely to be due to an enhancement of the collision cross section, which might be expected to scale with molecular size (i.e., ~ Z). Thus, we were led to consider other possibilities, such as a resonance or a bound state of the positron and the molecules. The spin-averaged lifetime of a positronium atom is τ_{ps} ~ 0.5 ns. Thus, we expect that if the resonance lifetime is of the order of τ_{ps}, the positron has unit probability of annihilation. Since the alkane studies were conducted at an N_2 gas pressue of 4.4 x 10^{-6}torr, we expect, based on the positron cooling studies described above, a characteristic cooling rate of less than 0.2 sec. Thus the positrons are quite cool--nearly at room temperature--during much of the time when the positron population is decaying exponentially.

MODEL OF THE POSITRON-MOLECULE RESONANCES[1]

Since τ is found to be insensitive to the background N_2 pressure, the binding appears to be due to a two-body process. Such processes have been discussed in the context of the binding of electrons to neutral molecules,[8,9] and we are led to a similar picture. The positrons have enough energy to directly excite low-energy vibrational modes in the large molecule, but they are not likely to excite electronic excitations in the molecule or to dissociate it. If we *assume* that the positron has an energy affinity, ε_A, for the molecule, then the incident positron energy plus some fraction or all of ε_A can be used to excite vibrational modes, in which case the positron will be attached to the molecule.

A reasonable explanation of the observed plateau in Z_{eff}/Z, shown in Fig. 4, when Z is increased beyond Z ≃ 74, is that, with increasing size, the lifetime τ_m of the complex has become comparable to the annihilation time ($\tau_m \simeq \tau_{ps}$). If we make this assumption, then we find a cross section of $\sigma \simeq$ 4 x 10^{-16} cm^2 for the binding of the positron and a molecule with Z = 74 (i.e., nonane, C_9H_{20}). Our measurements of the cooling of the positrons by the N_2 indicate that the inelastic, e^+-N_2 vibrational cross section is of the order of 0.5 x 10^{-17} cm^2. Thus, a value of 4 x 10^{-16} cm^2
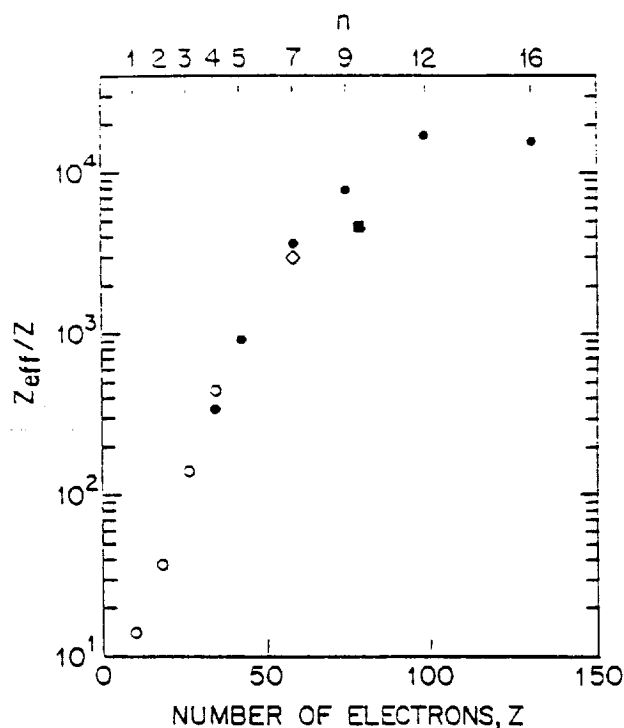

FIG. 5. The quantity Z_{eff}/Z for alkane molecules plotted as a function of the number of electrons, Z, in the molecule; Z_{eff}/Z is the annihilation rate per electron normalized by the Dirac annihilation rate expected in a free-electron gas. Filled circles are alkane data from the present work; open circles are from Ref. 3. The number of carbon atoms, n, in the alkane molecules studied is indicated by the upper scale. The solid square corresponds to decahydronapthalene ($C_{10}H_{18}$), and the open diamond to deuterated heptane (C_7D_{16}).

for C_9H_{20} does not seem unreasonable.

With the use of detailed-balance arguments[8] (commonly referred to as RRKM theory)[9], an expression for τ_m has been derived for the case of electrons bound to molecules. Adapted to the case of positrons, it can be written in terms of the positron affinity, ε_A, the incident positron energy, ε_i, the number, ℓ, of vibrational modes of the molecule, and their total zero-point vibrational energy, $\tilde{\varepsilon}_z$. In particular,

$$\tau_m^{-1} = (m_e/\pi^2 h^3)\, \varepsilon_i^{1/2}\, \tilde{\varepsilon}_z^{3/2}\, [\tilde{\varepsilon}_z/(\varepsilon_A + \tilde{\varepsilon}_z)]^\ell$$

$$\times\, \sigma(\varepsilon_i)\, I\,(\varepsilon_i, \varepsilon_z), \qquad (2)$$

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where $I(\varepsilon_i, \varepsilon_z)$ is a definite integral[8]; $\varepsilon = b\varepsilon_z$, with b a correction factor differing from unity by a few tens of percent;[9,10] and $\sigma(\varepsilon_i)$ is the excitation cross section discussed above.

There are two features of Fig. 5 which can be compared with Eq. (2) to yield estimates of the positron affinity ε_A—the plateau beginning at $Z = 74$ and the slope of $\ln(\tau_m)$ vs Z at small Z. Using Eq. (2) for our positron data at $Z = 74$ with $\varepsilon_i = 0.04$ eV, and assuming $\sigma(\varepsilon_i) = 4 \times 10^{-16}$ cm^2, $\ell = 81$ (corresponding to $Z = 74$), and $\tau_m = 0.5 \times 10^{-9}$ s, we find $\varepsilon_A/\widetilde{\varepsilon}_z = 0.15$. We now compare the slope of the curve in Fig. 5 at small values of Z to $d\ln(\tau_m)/d\ell$. Changes in Z are linearly proportional to changes in ℓ (i.e., $\Delta\ell = (9/8)\Delta Z$). Thus, the dominant dependence of $\ln(\tau_m)$ on Z will come from the $[\widetilde{\varepsilon}_z/(\varepsilon_A + \widetilde{\varepsilon}_z)]^\ell$ factor in Eq. (2), even if $\sigma(\varepsilon_i)$ and $I(\varepsilon_i, \varepsilon_z)$ have some ℓ dependence. The observed linear slope in Fig. 5 will occur only if $\varepsilon_A \propto \widetilde{\varepsilon}_z$, indicating that ε_A increases linearly with the size of the alkane molecule. On comparing the data to Eq. (2), we find $\varepsilon_A/\widetilde{\varepsilon}_z = 0.12$. For nonane with $Z = 74$, we estimate $\widetilde{\varepsilon}_z \simeq 6.8$ eV and assume $b \simeq 0.7$ (c.f., Ref. 10) to find that $\varepsilon_A \simeq 0.6 \pm 0.1$ eV.[11]

The sign of ε_A is assumed to be such that the positrons can form bound states with the molecules. However, energy is conserved in the two-body collisions studied here. Thus, the positrons are not bound, since this would require subsequent collisions to drain off the energy. Instead, they form resonances in which the positrons annihilate with increasing probability as the lifetime of the resonance increases. The data are consistent with the model presented here; however, it is clear that further work is necessary. In particular, it would be useful to have calculations of both the magnitude of ε_A and its dependence on molecular size for the case of positrons bound to alkane molecules.

In the model presented above, both the nature of the molecular vibrations, the vibrational density of states, and the positron affinity, ε_A, play an important role. We have now conducted a number of experiments to study the effect of different molecular species on the annihilation rate, A. In Table I, we present a summary of these results.

One test of the model is to change the nature of the molecular vibrations keeping the chemical species the same. We did this by measuring the value of A for a deuterated alkane and comparing this result with that for a protonated version of the same molecule. We expected that deuteration would lower the frequencies of a sizable fraction of the vibrational modes, thereby appreciably lowering ε_z, while keeping ε_A approximately the same. The result for heptane is A = 5.2± .5 torr^{-1} sec^{-1} for C_7D_{16} (shown as the open diamond in Fig. 5) as compared with A = 6.4 for C_7H_{16}. In contrast, Eq. (2) would predict that, for heptane, a 10% decrease in the frequencies of only 10% of the modes would *increase* A by a factor of 2.6. Thus the annihilation rate does not appear to be as sensitive as we would expect to the vibrational modes affected by the substitution of D for H. Neither the sign nor the magnitude of the effect is that which was expected.

Another possibility is that the low frequency modes are important in the binding process. With this in mind, the quantity A was measured for toluene (C_7H_8), a ring compound, and compared with that for heptane, the corresponding alkane, with the same number of carbons. The result was that A is the same for both molecules to within 20%. We also measured A for decahydronapthalene, $C_{10}H_{18}$, which is similar in chemical structure to the alkanes but has a "bridge" between two parts of the molecule, which we expected would eliminate some of the low frequency modes. As shown in Table I, the measured annihilation rate for $C_{10}H_{18}$ is a factor of 1.7 smaller than the 9-carbon alkane, nonane, and therefore even smaller with respect to the value expected for the corresponding 10-carbon alkane. The quantity Z_{eff}/Z for $C_{10}H_{18}$ is shown by the solid square in Fig. 5, and it appears to lie considerably below the alkane data.

In summary, the results of our tests of the effect on τ_m of changing the vibrational modes are mixed. We had expected deuteration to increase τ_m, and it did not. On the other hand, decahydronapthalene has fewer low-frequency vibrational modes than the corresponding 10-carbon alkane; and, from the physical picture presented, we might expect this to lower the probability of attachment. The data are consistent with this idea. It is clear that further work is necessary before we can claim to understand the formation of the positron-molecule resonances.

TABLE I

Annihilation Rate A (in torr^{-1} sec^{-1}) of Various Organic Molecules

		Z	A
butane	$C_4 H_{10}$	34	0.33
pentane	$C_5 H_{12}$	42	1.1
heptane	$C_7 H_{16}$	58	6.4
heptane (deuterated)	$C_7 D_{16}$	58	5.2
nonane	$C_9 H_{20}$	74	17
dodecane	$C_{12} H_{26}$	98	47
hexadecane	$C_{16} H_{34}$	130	59
glycerol	$C_3 H_8 O_3$	74	18
toluene	$C_7 H_8$	50	5.3
decahydronapthalene	$C_{10} H_{18}$	78	10
pump oil	–	–	90
sebacic acid methyl ester	$C_{12} O_4 H_{20}$	156	210

We have also measured the annihilation rate for glycerol ($C_3H_8O_3$), which, in contrast to the alkanes, has electron orbitals not involved in chemical bonding with appreciable electron density isolated from the nuclei. This molecule was measured to have a high value of A when compared to the alkane with a comparable number of carbon atoms. However, the value Z_{eff} for fixed Z is approximately that which we would expect from the alkane data.

Finally, we measured A for both "pump oil" and sebacic acid methyl ester; the latter is expected to be a chemically similar molecule to the oil. In both cases, A was larger than the largest alkane studied. It is likely that oil molecules are the source of the rapid positron annihilation rates observed in our early experiments which led to the study of the interaction of positrons and large molecules described here.

POSITIVE ION FORMATION

The existence of the long-lived resonances described above greatly enhances the probability that a positron will annihilate with an electron on the molecule. When this occurs, a positive ion of the same molecular species will result. We have directly observed the ions produced in this manner using the simple channel-plate electron multiplier as a detector in a time-of-flight mass spectrometer as described above.

Shown in Fig. 6 is the channel-plate signal as a function of time, τ, after the contents of the trap are dumped when butane (C_4H_{10}) is added to region III.[7] The signal at zero storage time, which is typical of that when no butane is added, shows a prompt peak at $t = 0$, corresponding to the trapped positrons, and a peak at 185 μs which corresponds to N_2^+. The N_2^+ ions are believed to be formed in region I, when the positrons ionize the N_2. This signal decreases monotonically as a function of storage time. Based on the simplest calculation using the applied potentials, the expected arrival time of the N_2^+ would be 170 μs, which is 9% lower than that measured. When CO_2 was introduced into the system, the expected arrival time was also 9% lower, and so the expected arrival times for all of the ions were scaled by this factor in order to identify the ion species detected.
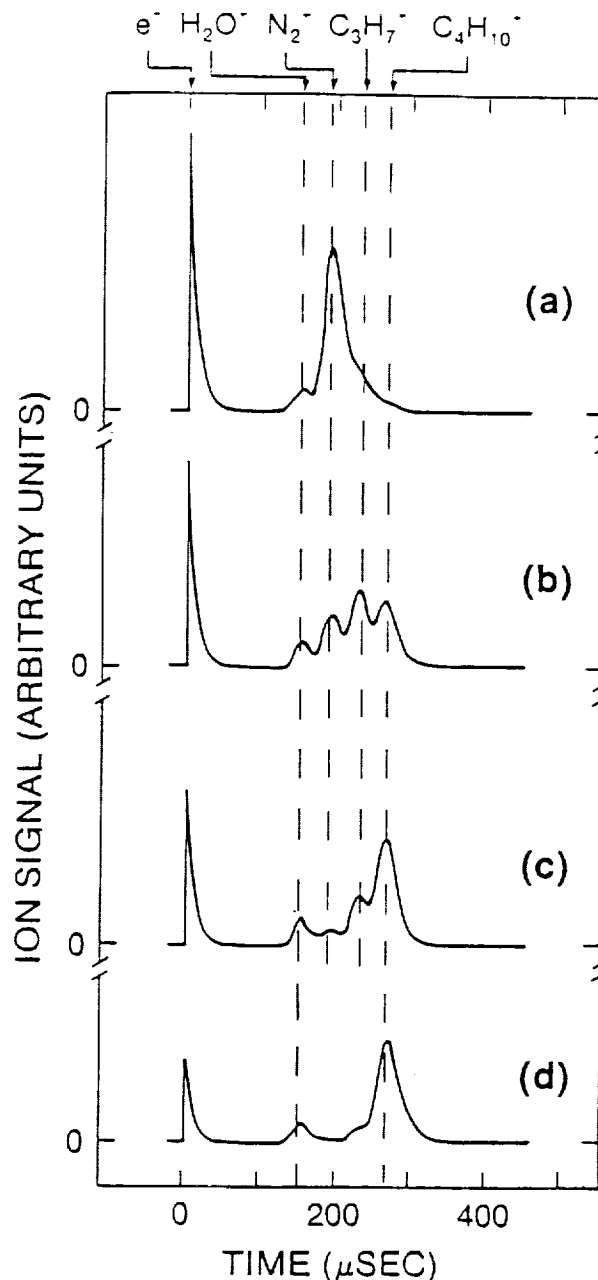

FIG. 6. Time-of-flight spectra of the ions observed when the positron trap is dumped, for the case where butane is added to region III. The traces correspond to storage times of (a) 0 s, (b) 0.5 s, (c) 1 s, and (d) 2 s. The filling time was 0.5 s, the N_2 pressure in region III was 0.5 x 10^{-7} Torr, and the butane pressure was 2.5 x 10^{-7} Torr. The identification of the peaks and their expected positions are indicated.

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In addition to the e^+ and N_2^+ signals, three other ion peaks are evident in Fig. 6. Our identification of these signals is indicated above the Figure. The decay time of the ion signals is strongly dependent on the applied magnetic field. This is consistent with estimates of the radial diffusion of these species out of the region where they are detected by the channel plate. In contrast, direct measurements of the radial distribution of the e^+ show that they do not diffuse appreciably on the time scale of the experiment.[4]

After about 1 s, the dominant ion peak occurs at 265 µs and corresponds to butane ions, $C_4H_{10}^+$. We have previously shown that the annihilation rate of the positrons is directly proportional to the C_4H_{10} density.[1] Thus, we would expect that the time dependence of the $C_4H_{10}^+$ could be described by the solution of the rate equations for the e^+ and $C_4H_{10}^+$, assuming that the population of each decays exponentially in time, with the first feeding the second (i.e., "parent-daughter decay" common in nuclear physics).[12] We have conducted such an analysis,[2] and we find that this model does explain the data.

The two other identifiable peaks in Fig. 6 appear to be H_2O^+ (150 µs) and $C_3H_7^+$ (235 µs).[13] Water is a likely impurity in our vacuum system and appears to play little or no role in the dynamics of the other species. The rise time and the amplitude of the $C_3H_7^+$ signal are consistent with it being generated by charge exchange between the N_2^+ and the butane, producing $C_3H_7^+$ and other products. We have carried out an analysis of the N_2^+ - $C_3H_7^+$ data similar to that described above for the e^+ - $C_4H_{10}^+$ data which supports this hypothesis.

Shown in Fig. 7 are data for the ions produced when heptane (C_7H_{16}) is added to region III. In this case, heptane ions are observed, but never as the dominant peak which appears to correspond to $C_4H_9^+$.[13] The previously observed N_2^+, H_2O^+, and $C_3H_7^+$ peaks are also evident. The $C_4H_9^+$ and $C_7H_{16}^+$ signals are approximately proportional to each other. They increase at early times as the positrons disappear in a manner similar to that described above for $C_4H_{10}^+$. These data indicate that the positrons can breakup large molecules into fragments. The details of this process remain to be studied.
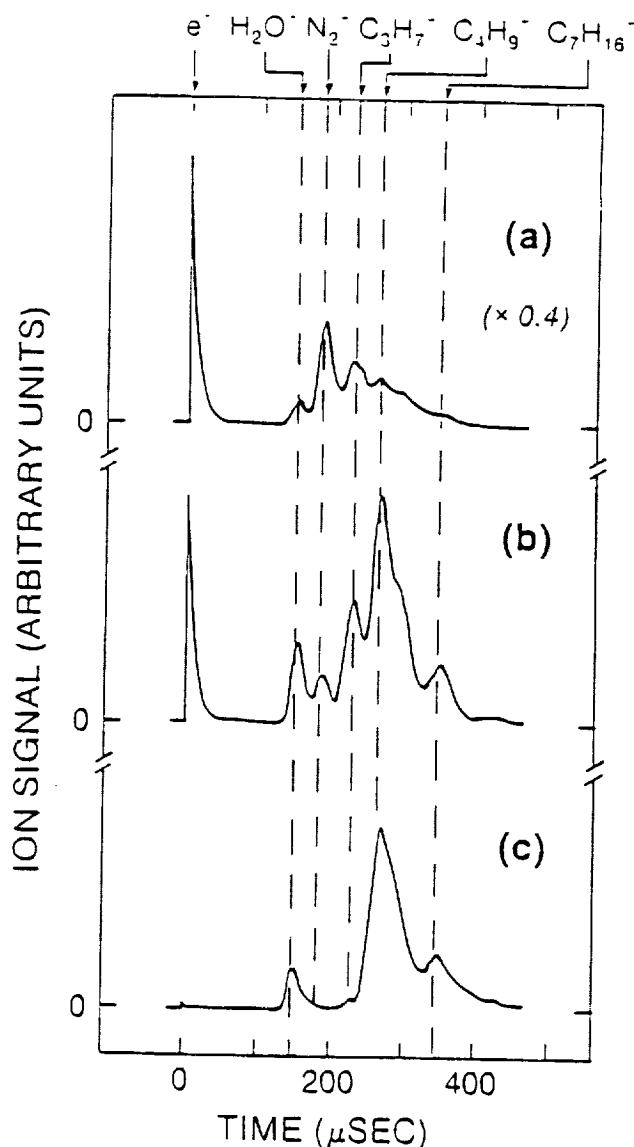

FIG. 7. Time-of-flight spectra of the ions observed when the trap is dumped, for the case where heptane (C_7H_{16}) is added to the trap: The storage times are (a) 0.5 s, (b) 2 s, and (c) 4 s. The filling time was 0.2 s in (a) and 1 s in (b) and (c). The identification of the peaks and their expected positions are indicated.

The results presented here show that positrons can be used to form positive ions from large neutral molecules. Because of the formation of long-lived e^+-molecule resonances, the cross sections for these processes are much larger than previously anticipated. Since the ion formation process is qualitatively different than conventional techniques for forming positive ions, it may be useful in obtaining additional information about unknown molecular species when these molecules are studied using mass spectrometry. It is also possible that more detailed studies of the specific ions formed from a given molecule after positron annihilation may give insight into the nature of the e^+-molecule resonances themselves.

SUMMARY

We have presented data for the annihilation rate of room-temperature positrons in the presence of a combination of N_2 and large organic molecules. The large annihilation rates which we observed have led us to conclude that the positrons form long-lived resonances with the organic molecules. These resonances are formed in two-body collisions. If there were a third body to carry away the excess energy, true bound states would be formed. In any case, however, the lifetime of the complex is limited to about 1 nsec, due to annihilation of the positron with an electron on the molecule.

We have discussed a model for the formation and the lifetime, τ_m, of these resonances. The model indicates that, for the alkanes, the positron-molecule affinity ε_A is proportional to the size of the molecule, and that, for nonane, $\varepsilon_A \simeq 0.6$ eV. Specific tests of the model using different chemical species and comparing deuterated and protonated alkanes produced mixed results. It is clear that more work in this area is warranted.

Finally, we have observed the positive ions produced when a positron annihilates in one of these resonances. This is a qualitatively new and different method of positive ion production. Details of this process and its potential applications to mass spectrometry warrant further study.

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9. See, for example, W. Forst, *Theory of Unimolecular Reactions* (Academic Press, New York, 1973); and W. Forst, Chemical Reviews **71**, 339 (1971).

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11. This value of ε_A is in the lower end of the range of values quoted in Ref. 1. The difference is due to the correction of a numerical error in the plateau calculation and to improved estimates of both ε_z and b, which are now taken to be smaller than the values previously assumed.

12. See, for example, W. R. Leo, *Techniques for Nuclear and Particle Physics Experiments* (Springer-Verlag, New York, 1987).

13. The data are not of sufficient resolution to determine the precise numbers of hydrogen atoms in these ions, so the numbers of hydrogen were chosen based on what are likely to be stable ions [K. Raghavachari (private communication)].